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## Mechanical Behavior of Polymer Nanocomposites : a discrete simulation approach

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### ABSTRACT

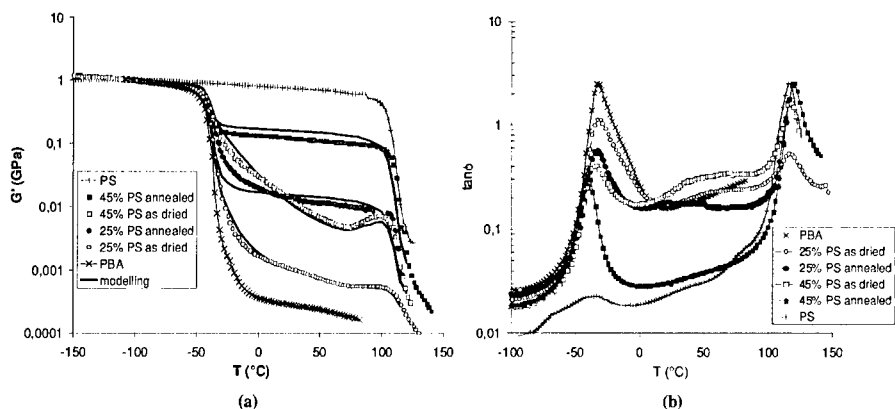
This work reports the dynamic mechanical characterization of nanocomposites based on a poly(butyl acrylate) matrix filled with spherical particles of either polystyrene or silica both of diameter around 100 nm. A discrete numerical simulation, taking into account the microstructure and the nature of contact between reinforcing particles has been developed. This simulation enables to quantify the effect of interactions between filler particles on the elastic modulus, and in a more general sense, to clarify the concept of mechanical percolation. It gives results in very good agreement with experimental data.

### INTRODUCTION

Nanocomposite materials consist of a nanometer-scale phase in combination with another phase acting as a matrix. Work about polymer nanocomposites has exploded over the last few years. Their properties are reported to be different from that of their micro-scale counterparts [1,2]. The specific features in nanocomposites are (i) the large interfacial area which can reach 100-1000 m<sup>2</sup>/g, (ii) the average distance between particles, down to a value comparable with the macromolecule coils. This can favor the short-distance filler-filler interactions leading, above a threshold fraction, to the formation of a network (percolation). Moreover, the presence of an interphase polymer layer near the inorganic surface with properties differing dramatically from the bulk polymer is often assumed. Due to the large surface area of the nanofillers, the interphase polymer is expected to dominate the properties of the nanocomposites. Though significant progress has been made in developing nanocomposites with different polymer matrices, a general understanding has yet to emerge. A major challenge to further development of nanocomposites is the lack of structure - properties modeling taking into account the influence of filler-filler and filler-matrix interactions.

### MATERIALS AND EXPERIMENTAL RESULTS

Nanocomposites materials were prepared using the emulsion polymerization route. PS and PBuA latexes were blended varying the PS content (from 10 to 45 vol. %). After film formation (35°C, 90 % of relative humidity), this process leads to rigid spherical PS fillers (d=110nm) randomly dispersed in a soft PBuA polymer matrix (these films are referred as "as dried" films). When PS-PBuA films have undergone an annealing treatment at 140°C (i.e. above the glass transition of the PS) for several hours, films were designated "annealed". Silica particles (Stöber synthesis [3]) with similar diameter (125 nm) were also introduced in the same PBuA matrix.



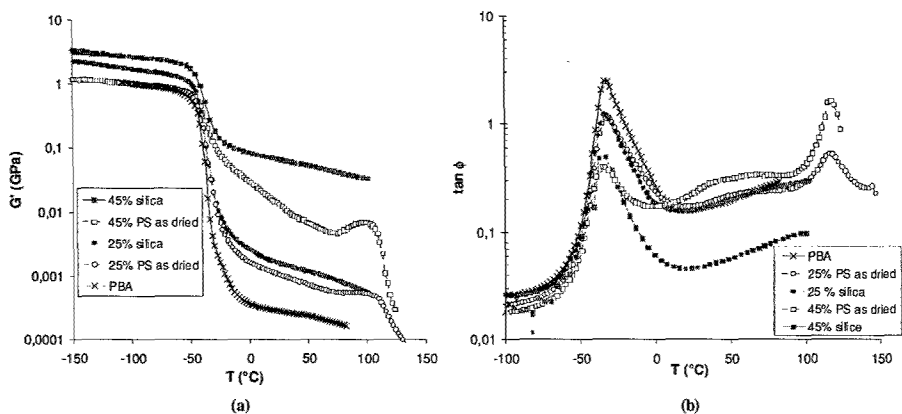
**Figure 1:** (a) Elastic shear modulus of “as dried” and “annealed” PS/PBuA nanocomposites versus temperature (1 Hz, 1°C/min). Lines: modeling using the discrete numerical simulation.

(b) loss factor of “as dried” and “annealed” PS/PBuA nanocomposites against temperature

Dynamic mechanical analysis of the samples have been performed in torsion [4] in the temperature range [-170; 150 °C] with a heating rate of 1°C/min at a fixed frequency of 1 Hz.

**Figure 1a** shows the temperature dependence of the storage shear modulus of the PS and PBuA phases and of various PS-PBuA composites. The behavior of “as dried” films can be described as follows: (i) a glassy plateau where the modulus of both phases and composites films are about 1 GPa; (ii) above the  $\alpha$  relaxation of the PBuA (-50°C), a large drop in modulus followed by a continuous decrease and (iii) around 70 °C, an increase of the modulus until the PS main relaxation. These two counteracting phenomena lead to the presence of a bump in the loss factor curve, located between the peaks associated to the main relaxation of PBuA and PS phases (**Figure 1b**). Above -50°C, at a given temperature, the modulus is observed to strongly increase with the filler content. In the case of the “as dried” nanocomposites, the dependence of  $G'$  with temperature in the range [-50; 70°C] is more pronounced when the filler content is higher. After the annealing treatment, the PS/PBuA nanocomposites exhibit a much higher modulus (compared to as dried) with temperature dependence very close to that of the PS at the same temperature. These results are thought to be the consequence of the formation of a stiff network of PS. Actually, in the case of spherical filler, the percolation threshold is about 20 vol. %. Thus, before annealing (“as dried” samples), for filler content above 20 vol.%, a percolated network of filler is likely to be present in the sample but the interactions between the particles are probably softer, even punctual. Thus, these experimental results feature the difference between geometrical and mechanical percolation.

In the case of silica (**Figure 2**), the dependence of the modulus on filler content is observed in both the glassy and the rubbery plateaus since the shear modulus of silica is about 30 times that of the glassy polymer. Above the main relaxation of the PBuA, silica-filled



**Figure 2:** (a) Elastic shear modulus and (b) internal friction of “as dried” PS/PBuA nanocomposites and silica/PBuA nanocomposites as a function of temperature (1 Hz, 1°C/min).

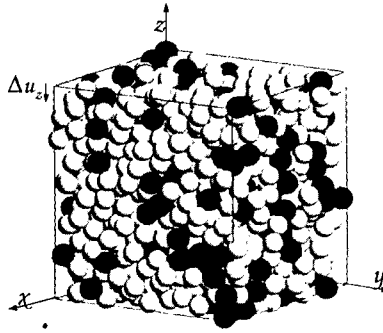
nanocomposites display higher moduli than that filled with PS. This can be attributed to the presence of hydrogen bonds assumed to take place between silica particles (instead of Van der Waals bonds in the case of PS). Moreover, the modulus increase around 70°C is no longer observed in the case of silica filler. That indicates that this phenomenon has to be related to the interactions existing between PS fillers (and/or between PS and PBuA) and that these interactions are temperature-dependent.

To sum up, the mechanical behavior of the PS-PBuA and Silica-PBuA nanocomposites in the rubbery plateau is ruled by the filler content and the strength of the contacts between particles.

## DISCRETE NUMERICAL APPROACH

Experimental results have shown a major influence of the nature of interactions between fillers on the linear mechanical behavior. In that case, classical homogenization methods based on mean field-type approximations fail to predict the modulus increase. As a consequence, we have developed a discrete numerical approach based on a composite assembly of spherical particles, which explicitly takes into account the microstructure and the nature of contact between reinforcing particles.

This model, described in detail in [5], is in fact based on the scheme developed by Jagota [6] to model the viscosity of composite packing of hard and soft spheres. Calculations are made on a close packing of monodisperse spheres, which represent either the filler particles or the PBuA matrix particles ( $\approx 1000$  spheres with a packing density  $\approx 0.57$ , **Figure 3**). At each contact between neighboring spheres, three forces and three moments are transmitted. These efforts are expressed as a linear function of the displacements and the rotations of the connected spheres, exhibiting different “contact stiffness” (normal, tangential, flexural and torsion). These



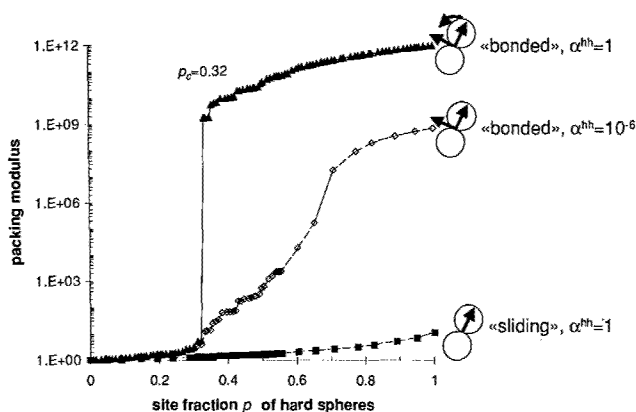
**Figure 3:** Example of random packing of monodisperse hard and soft spheres used to calculate the effective modulus.

stiffness depend both on the modulus of each connected sphere and on a geometrical parameter  $\alpha$  defined as  $\alpha=(R_c/R)^2$ , where  $R_c$  and  $R$  are the contact radius and the sphere radius respectively. In fact, the larger  $\alpha$  (i. e. the contact area), the higher the transmission of moments through the contact.

Three kinds of contact are thus considered: soft/soft, hard/hard and soft/hard contacts.  $\alpha^{ss}$  for soft/soft contacts is taken equal to 1, since the PBuA matrix of nanocomposites materials is continuous. For hard/hard contacts, we used a variable  $\alpha^{hh}$  in order to quantify the effect of the strength of filler-filler interactions on the effective modulus. Soft/hard contacts result from a serial law between hard/hard contacts (with  $\alpha^{hh}=1$  since the PBuA matrix totally wets filler particles) and soft/soft contacts ( $\alpha^{ss}=1$ ). The effective modulus is then numerically deduced by applying adequate boundary conditions, corresponding to a compression test.

### Simulation results

The evolution of the packing modulus with the site fraction  $p$  of hard inclusions is plotted in **Figure 4** considering, in a first time, a huge contrast between soft and hard particles:  $G_r/G_m=10^{12}$ . When filler-filler interactions are strong (so called "bonded" case with high contact area:  $\alpha^{hh}=1$ ), the effective modulus increases suddenly at the geometrical percolation threshold  $p_c=0.325$ . On the other hand, when filler-filler interactions are weak ("bonded" case with  $\alpha^{hh}=10^{-6}$ ), i. e. when the rolling of hard particles is allowed, there is no discontinuity at the percolation threshold. Moreover, the modulus obtained for 100% of hard particles is lower than the modulus of bulk filler. Like in reference [6], we have also defined a "sliding" contact, where hard/hard contacts resist only to normal efforts with the properties of filler material, the others efforts being transmitted like in soft/soft contacts. **Figure 4** shows that in that case, the effective modulus increases only a little: the packing behaves like a sand pile.



**Figure 4:** Evolution of the packing modulus as a function of the site fraction  $p$  of hard spheres for different cases of hard/hard contacts (1000 spheres,  $G_r/G_m=10^{12}$ ).

This simulation shows clearly the differences between geometrical percolation and mechanical percolation: the mechanical percolation occurs only when filler-filler interactions are strong enough (transmission of moments). In contrast, when filler-filler interactions are weak, the contribution of the formation of a macroscopic filler network has little effect on the modulus.

#### Application to PS/PBuA nanocomposites

This model has been applied to PS/PBuA nanocomposites. After the annealing treatment, PS particles are strongly bonded. As a consequence, calculations have been made with  $\alpha^{hh}=1$  (efforts and moments are transmitted as in bulk PS). Simulation results plotted in **Figure 1** are in very good agreement with experimental data. Before the annealing treatment, the strength of filler-filler contact is unknown and evolves with temperature. Therefore, the variation of  $\alpha^{hh}$  with temperature has been adjusted in order to agree well with the experimental data for the nanocomposite containing 25% PS. Then, keeping the same law for  $\alpha^{hh}(T)$ , calculations have been made for 45% PS. As shown on **Figure 1**, the prediction is very close from experimental result.

#### CONCLUSIONS

The main influence of the presence of the nanosized filler in a poly(butyl acrylate) matrix are observed in the rubbery plateau. In this temperature range, the contrast between the modulus of the different phases is huge and the mechanical behavior seems to be essentially governed by the microstructure and the strength of the links between the filler, these links being either direct contacts or indirect contacts via the matrix in between. To account for the observed increase of modulus and its evolution with temperature, a discrete model of spheres assembly taking into account the local filler/filler and matrix/filler contacts is proposed. This approach agrees well

with the experimental data and allows to better understand the reinforcement when the percolation threshold is crossed.

## ACKNOWLEDGEMENTS

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